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"Multiscale Capabilities for Exploring Transport Phenomena in Batteries": Ab Initio Calculations on Defective LiFePO4

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Disclaimer

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Final Subcontract Report : "Multiscale Capabilities for Exploring Transport Phenomena in Batteries": Ab initio calculations on defective $LiFePO_4$

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Under the direction of Ming Tang and Brandon Wood,
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Summary of the work performed

We have began the project "Multiscale Capability for Exploring Transport Phenomena in Battery", which is sponsored by Laboratory Directed Research and Development Program at Lawrence Livermore National Laboratory in February 2012 as the subcontract was approved. We have been performing first-principles quantum-mechanical calculations to first establish the general modeling framework. It was found that it is essential to employ advanced Density Functional Theory (DFT) calculations with Hubbard U correction, in order to describe the battery material, in particular, $LiFePO_4$ (Figure 1). The presence of localized d-electrons at Fe ion sites requires the better treatment of non-local correlation beyond that of standard DFT.

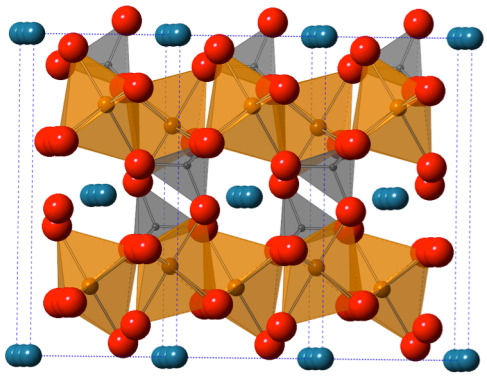

Figure 1: Optimized $LiFePO_4$ using DFT+U calculations, with tetrahedral and octahedral cages shown.

As our aim was to first identify and investigate key transport/reaction mechanisms affecting the performance of Lithium-ion based batteries, we have began out work by characterizing the standard structures and how the defects influence the important electronic structure. The resulting electronic structure is under investigation in order to obtain important insights.

These investigations are driven by the fact that almost all first-principles work have been done on an ideal and perfect $LiFePO_4$. At the same time, there is growing experimental evidence that imperfections such as vacancies and antisites play key roles in limiting the battery operation.

Details of our calculations and findings

We performed state-of-the-art Density Functional Theory (DFT) Calculations in the plane-wave pseudo-potential formalism. In particular, we used the advanced Hubbard correction to the generalized gradient approximation for the exchange-correlation effects. Ultrasoft pseudo-potentials were used to described core-valence interactions, and the plane-wave cutoff of 70 Ryd was used to converge the total energy. The simulation cell contains 224 atoms, and 2x2x4 k-

points are use in Brillouin Zone integration. The variable-cell optimization was performed to accurately determine the bulk properties such as the lattice constant.

Hubbard correction to DFT for taking into account the d-electron correlation was found important for describing anti-ferromagnetic nature of Fe sites. In electronic structure calculations, the magnitude of hubbard U value was determined using the linear-response theory. The U value depends on the oxidation states of the iron, and they were determined to be 3.7 eV and 4.9 eV for Fe(II) and Fe(III), respectively.

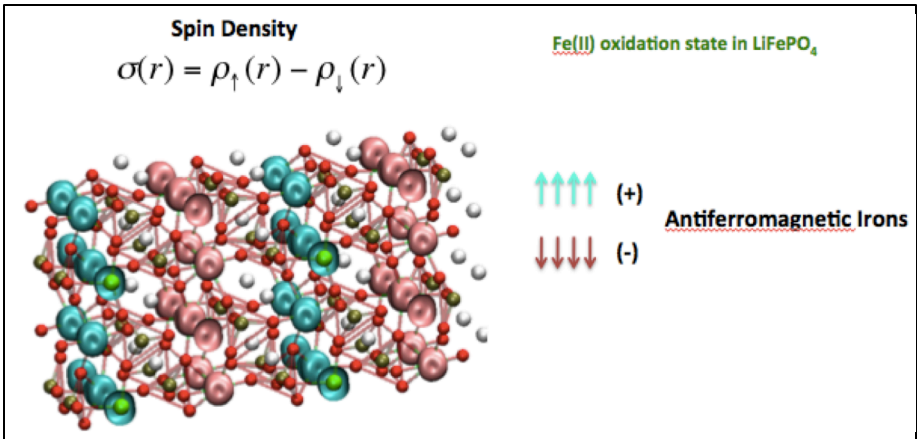

Figure 2: Spin density distribution in $LiFePO_4$, showing the anti-ferromagnetic nature. Green atoms are irons, white atoms are lithium, red atoms are oxygen, and brown atoms are phosphorus.

Our calculations show that the magnetization of 3.99 Bohr Mag. per unit at Fe. This magnetization increases to 4.92 Bohr Mag. per unit, upon complete Lithium depletion. Fe(II) oxidation state in $LiFePO_4$ becomes Fe(III) in $FePO_4$, consistent with the conventional understanding of Li being effectively ions in $LiFePO_4$. Figure 2 shows the spin density, defined as the up-electron density minus the down-electron density, distribution of in $LiFePO_4$.

Investigation of these detailed electronic structure changes with defects such as Li vacancy and Li-Fe antisite vacancies was underway, as they will have important impact in Li diffusion. Influence of the strain was also being studied, especially to correlate the energetic effects to the changes at the electronic structure level.

Presentations

The results from this project were presented as part of the invited talk at Chemistry Department Colloquium at North Carolina State University “Materials Challenges for Energy Conversion: Insights and Predictions from First Principles Dynamics” (9/29/2012).